

Dissociations of Positively Charged Aliphatic Epoxides.

I. Structure Elucidation of the γ -Cleavage Products

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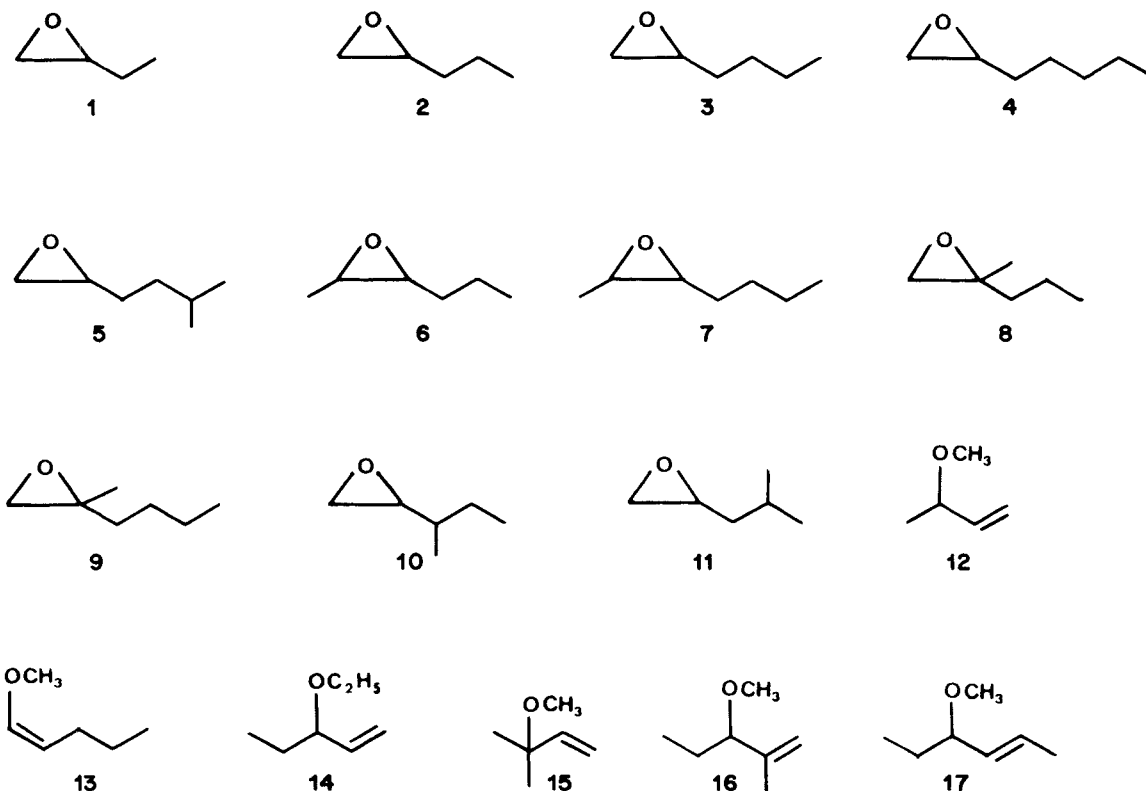
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Dissociative ionization of 1,2-epoxy *n*-alkanes gives rise to abundant $[C_4H_7O]^+$ ions of structure $[CH_3OCHCHCH_2]^+$. This conclusion is drawn from metastable ion analysis and from collisional activation spectra. This fragmentation involves the C—C ring opening and a 1,4-H migration leading to the corresponding enol ether $[CH_3OCHCHCH_2R]^+$ precursor of $[CH_3OCHCHCH_2]^+$ fragment. The same isomerization scheme applies to 1,2-epoxy methyl substituted alkanes and 2,3-epoxy *n*-alkanes.

Twenty years ago, Brown, Kossanyi and Djerassi presented a thorough examination of the mass spectra of 24 aliphatic epoxides.¹ They observed that, in most cases, cleavage of the γ -bond remote from the ring was the process of greatest importance in the source of the mass spectrometer. In the case of epoxide of terminal unbranched alkenes, this γ -cleavage is responsible for the peak m/z 71, the high-resolution mass measurements demonstrating the composition of the ion to be $[C_4H_7O]^+$. Furthermore, in the mass spectra of 4,4-*d*₂-epoxyhexane and 5,5-*d*₂-epoxyhexane, the corresponding peaks appear at m/z 73 and 71 respectively.

Several mechanisms were proposed to account for these observations but no definite choice has been possible due to the lack of methods for characterizing the structure of fragment ions. In the present study, the mass-analysed ion kinetic energy (MIKE) spectra and collisionally activated dissociation (CAD) spectra are used in order to determine unambiguously the structures of the γ -cleavage products of epoxides 1-11.

As established below, the corresponding $[C_4H_7O]^+$ and $[C_5H_9O]^+$ ions structures may be also produced by dissociative ionization of unsaturated ethers 12-17.



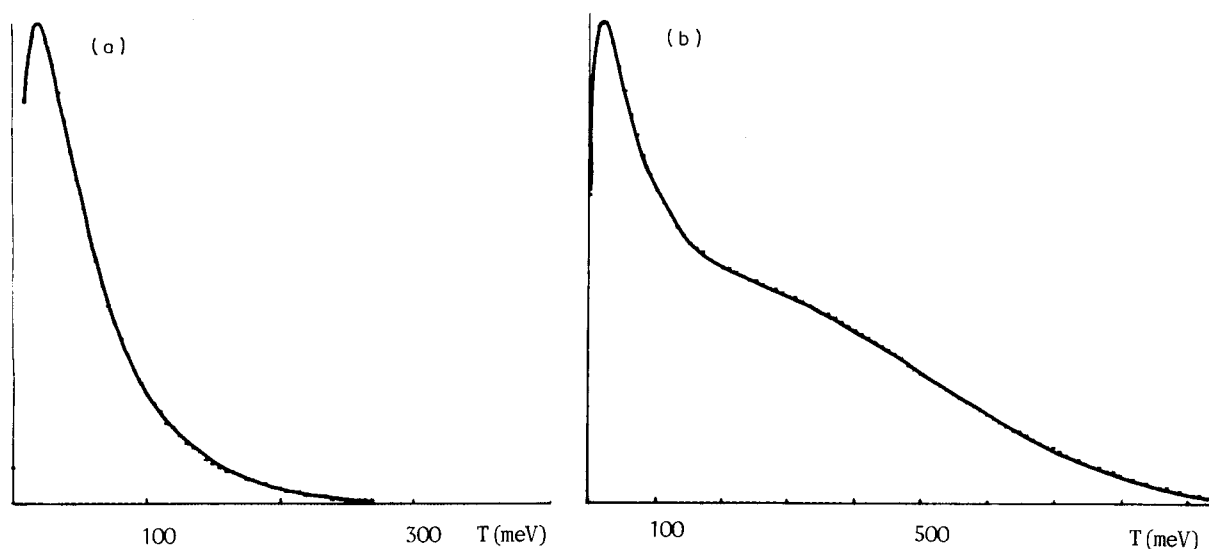


Figure 1. Distribution of kinetic energy release for $[C_4H_7O]^+$ (a) $m/z\ 71 \rightarrow m/z\ 41$ (b) $m/z\ 71 \rightarrow m/z\ 43$.

RESULTS AND DISCUSSION

The γ -cleavage of 1,2-epoxy *n*-alkanes

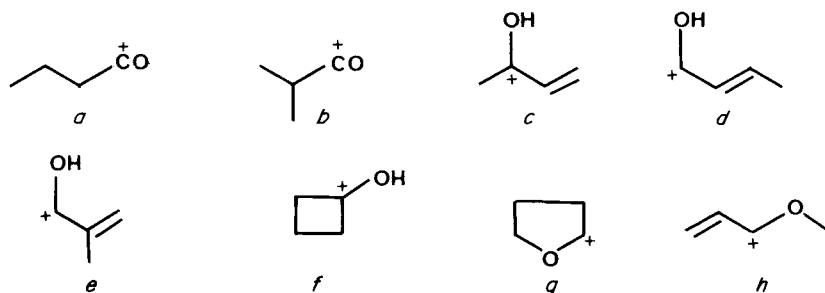
Structure of the $[C_4H_7O]^+$ ions. The MIKE spectra of $m/z\ 71$ originating from dissociation of ionized **1–5**, **12** and **13** are identical. They contain three peaks: $m/z\ 53$, 43 and 41 . The base peak corresponds to the loss of 30 daltons, its profile is simple Gaussian. The loss of 28 daltons gives rise to a slightly less intense peak of composite profile. Finally, the loss of 18 daltons is associated with a minor signal (about 10% of the total ion current).

The distributions of kinetic energy release, $n(T)$, are reproduced in Fig. 1.

Identical spectral features are obtained for the seven precursors thus indicating a unique structure for the $[C_4H_7O]^+$ ions.

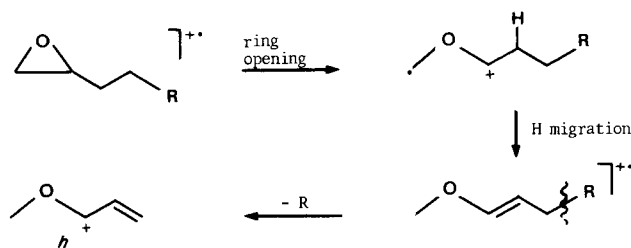
On the other hand, these results may be compared to the MIKE spectra of $[C_4H_7O]^+$ ions of known structure. On this basis one must exclude acylium ions *a* and *b*, hydroxy-carbenium ion *e* and the β -protonated 2,3-dihydrofuran *g*: their MIKE spectra exhibit only one peak at $m/z\ 43$.^{2–5} In a similar manner, neither ions *c*, *d* or *f* yield a fragment ion at $m/z\ 41$ in their metastable decompositions.⁶

Clearly the dissociation of **1–5**, **12** and **13** leads to another structure. The most reasonable proposition is ion *h* which can be obtained by direct bond cleavage from both **12** and **13**. One may note that this suggestion is also supported by the preponderance of the transition:



The CAD-MIKE spectra of $[C_4H_7O]^+$ ions coming from **1–5**, **12**, **13** are reported in Table 1. They show that the same structure (or mixture of structures) represents the undecomposed $[C_4H_7O]^+$ ions for the seven precursors. Our data agree also with a similar experiment using dimethylacetal as precursor.⁷

Mechanism of formation of $[C_4H_7O]^+$. The formation of the methoxy carbenium ion $[h]^+$ from epoxides **1–5** may well be accounted for by the mechanism summarized in Scheme 1. The first step is the opening of the epoxide ring along the C–C bond, which is followed by a 1,4 H-transfer giving an α,β -unsaturated ether precursor of $[h]^+$:



Scheme 1

This mechanism is supported by separate experimental and theoretical evidence. It was recently established that the open form of ethylene oxide radical cation

Table 1. CAD-MIKE spectra of $[C_4H_7O]^+$ ions^a

Precursors m/z	70	69	56	55	53	45	43	42	41	40	39	38	37	31	29	27	15
1	(260) ^b	17	45	36	(43)	7	(80)	21	(400)	17	100	25	11	9	48	70	17
2	5	20	28	40	(35)	7	(60)	21	(390)	17	100	26	13	7	44	61	13
3	7	18	27	37	(25)	7	(40)	23	(340)	17	100	25	12	8	45	64	15
4	9	18	25	38	(24)	8	(49)	22	(330)	17	100	27	11	9	47	70	18
5	7	18	25	38	(28)	7	(58)	22	(350)	17	100	26	12	8	48	69	16
12	7	16	25	35	(29)	7	(40)	21	(350)	17	100	27	12	8	44	65	16
13	3	19	27	37	(38)	7	(52)	18	(470)	18	100	27	13	9	48	67	17

^a The peaks with bracketed abundances appear also in the unimolecular dissociation spectra.

^b Not meaningful, overlapping with m/z 71 parent peak.

is more stable than the ring closed form by 80 kJ mol^{-1} .^{8,9} Moreover, the barrier to ring opening is predicted by *ab initio* calculations to be less than 15 kJ mol^{-1} .⁹

Experimental results are also best explained by the occurrence of ring opening for ethylene oxide^{10,11} and propylene oxide¹² molecular ions.

This thermodynamic aspect is illustrated by Fig. 2 in the case of compound 2. The heat of formation of $[2]^+$ (846 kJ mol^{-1}) is calculated using $\Delta H_f^0 [2] = -133 \text{ kJ mol}^{-1}$ ¹³ and ionization energies $IE(2) = IE(1) = 10.15 \text{ eV}$.¹⁴ The open structure $[2a]^+$ is assigned 80 kJ mol^{-1} lower in energy than $[2]^+$ by reference to the *ab initio* calculation on ionized ethylene oxide.^{8,9} Substitution on one of the C atoms by a propyl group should afford an overstabilizing effect, thus 766 kJ mol^{-1} constitutes certainly an upper limit for $\Delta H_f^0 [2a]^+$.

The $\Delta H_f^0(2b) = -175 \text{ kJ mol}^{-1}$ ¹³ combined with an $IE(2h) \approx IE(\text{dihydropyrane}) = 8.37 \text{ eV}$ ¹⁵ give $\Delta H_f^0 [2b]^+ \approx 630 \text{ kJ mol}^{-1}$.

The ΔH_f^0 of the fragment ion $[CH_2CHCHOCH_3]^+$, $[h]^+$, is estimated to be 630 kJ mol^{-1} on the basis of $\Delta H_f^0 [CH_2=CH-CHOH]^+ = 659 \text{ kJ mol}^{-1}$ ¹⁶ and subtracting 29 kJ mol^{-1} for the OH/OCH₃ substitution

as in the system of saturated homologue $[CH_3CHOH]^+/[CH_2CHOCH_3]^+$.¹⁷

The major feature of the potential energy profile sketched in Fig. 2 is that the two intermediate states $[2a]^+$, $[2b]^+$ and the fragments $[h]^+ + CH_3$, all lie below the energy level of the molecular ion $[2]^+$. With the near absence of an energy barrier for ring opening (TS 1 < 855 kJ mol^{-1} , assuming a behaviour of $[2]^+$ comparable to ethylene oxide^{8,9}) and if TS 2 is also lower in energy than 855 kJ mol^{-1} , the profile accounts for the lack of molecular peaks in the mass spectrum of 2. This observation is valid for all the compounds studied with the exception of 1.

The γ -cleavage of 1,2-epoxy methyl substituted alkanes and 2,3-epoxy *n*-alkanes

Predicted mechanism of dissociation. If the mechanism proposed in Scheme 1 is also correct for 6–11, one would expect the γ -cleavage to yield fragment ions $[C_3H_5O]^+$. The structure of these may be predicted to be *i*, *j*, *k* or *l* (Scheme 2) alkoxy carbenium ions.

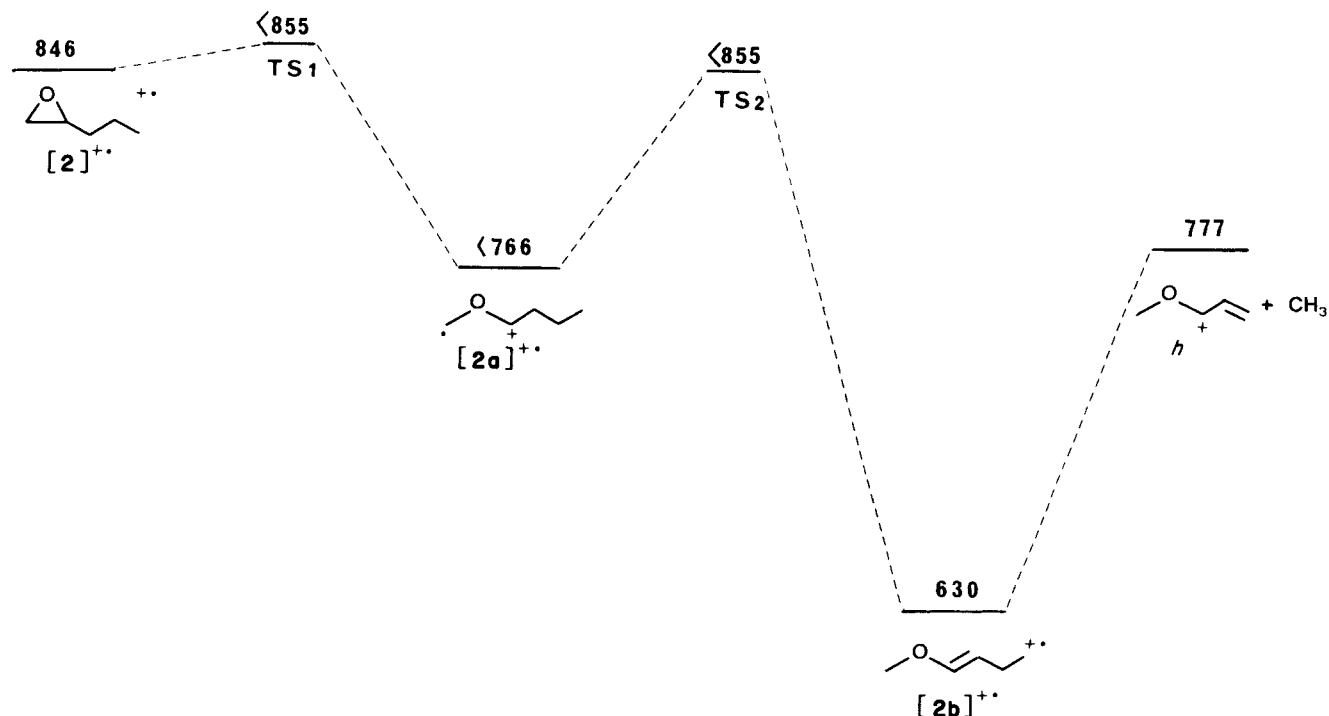


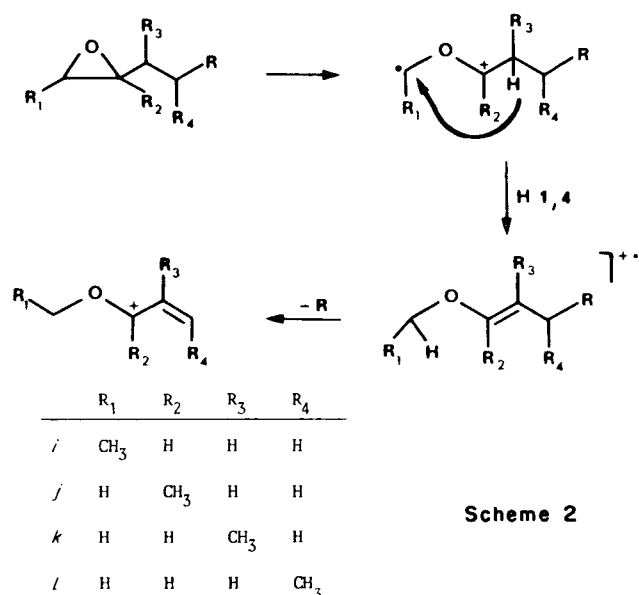
Figure 2. Suggested potential energy profile of 1,2-epoxypentane.

Table 2. CAD-MIKE spectra of $[C_5H_9O]^+$ ions^a

Precursors m/z	84	83	70	69	67	57	55	53	51	50	45	43	41	39	31	29	27	15
14	11	16	—	7	(4)	(1130)	75	3	—	—	9	(27)	10	43	13	100	61	1
6 <i>i</i>	8	10	—	8	(15)	(872)	73	2	—	—	9	(12)	10	43	12	100	59	—
7	5	11	—	7	(4)	(1034)	59	2	—	—	11	(11)	10	43	12	100	63	1
15	16	39	21	17	(23)	(11)	(823)	79	32	—	32	(199)	30	100	4	40	88	14
8 <i>j</i>	9	28	13	21	(8)	(9)	(677)	73	27	—	34	(153)	32	100	2	41	81	14
9	10	43	23	12	(17)	(33)	(850)	64	35	—	43	(263)	31	98	4	37	100	16
16	9	13	6	32	(4)	(13)	(555)	44	13	12	18	(25)	56	100	2	44	31	8
10 <i>k</i>	11	12	7	38	(12)	(48)	(536)	52	15	15	28	(38)	53	100	3	46	40	9
17	28	3	8	64	(3)	(3)	(280)	72	15	13	47	(7)	49	100	3	38	40	8
11 <i>l</i>	18	12	8	57	(3)	(5)	(220)	69	14	14	47	(14)	51	100	2	40	47	10

^a The peaks with bracketed abundancies appear also in the unimolecular dissociation spectra.

These four structures may be also generated by dissociation of the unsaturated ethers 14–17.



Scheme 2

Structures of $[C_5H_9O]^+$ ions. Ions *i* are clearly distinguishable from their isomers *j*, *k* and *l*. The MIKE spectra of $[C_5H_9O]^+$ ions from 14, 6 and 7 are dominated by the loss of 28 daltons ($\langle T \rangle = 65$ meV, simple Gaussian), two minor peaks appear at m/z 67 and 43. In the cases of precursors 8–11, 15–17, the major peak in the MIKE spectra of $[C_5H_9O]^+$ ions is m/z 55, and three small contributions to the ion current appear at m/z 67, 57 and 43. The distribution of kinetic energy release shows only slight differences for the process m/z 85 \rightarrow m/z 55. In all the cases the profile is simple Gaussian with a mean T value situated between 60 and 90 meV.

Table 2 contains the CAD-MIKE spectra of $[C_5H_9O]^+$ ions from 6–11, 14–17. Once again the peculiar behaviour of ion *i* is apparent. It is clear also that 14, 6 and 7 lead to the same fragment ion *i* in agreement with the proposed mechanism (Scheme 2).

Ion structure *j* (precursors 15, 8 and 9) is also unambiguously characterized by its CAD-MIKE spectrum. Important signals are observed at m/z 83, 70, 53, 39 and 27. The absence of a peak at m/z 50 is in contrast with structures *k* and *l*. For these two (precursors 16, 10, and 17, 11 respectively), the structure assignment is not so obvious. Nevertheless careful examination of CA spectra in the mass range 39–45 and 67–70 allow a

characterization of *k* and *l*. For example, the ratio m/z 41: m/z 45 is 1.5 for *k* and only 0.8 for *l*. One may observe also a higher intensity for m/z 69 in the case of *l*.

Note that in the case of 6 and 7 two 1,4-H migrations are possible from the open forms, one involves a primary hydrogen, the other a secondary one. Only the latter transfer is observed as indicated in Scheme 2. The former would give vinyl-butyl ether (from 6) or vinyl-pentyl ether (from 7) which are precursors of m/z 85 of 3-methyl-2-tetrahydrofuran structure.¹⁸

In summary, the predictions established from Scheme 2 seem to explain correctly the behaviour of ionized epoxides 6–11.

CONCLUSION

The present study demonstrates that the major trends in the chemistry of the molecular radical-cation of aliphatic epoxides are explicable in terms of an initial C–C ring opening. This initiation step leads to a highly stabilized intermediate which may support energy-requiring rearrangement processes. In this context, occurrence of 1,4-hydrogen migration is attested for epoxides 1–11 but also for a majority of $[C_5H_{10}O]^+$ and $[C_6H_{12}O]^+$ isomeric epoxides.¹⁹

EXPERIMENTAL

All the epoxides (1–11) were synthesized from the appropriate alkenes using metachloroperbenzoic acid in CH_2Cl_2 .

The methyl ethers 12, 15, 16 and 17 result from the alkylation of the corresponding alcohol using CH_3I and powdered KOH stirred in DMSO.²⁰ The starting alcohols for preparation of 16 and 17 was obtained from C_2H_5Br and respectively crotonaldehyde and methacrolein by Grignard synthesis.

The ethyl ether 14 comes from the corresponding alcoholate and C_2H_5I .

The MIKE and CAD spectra were recorded on a VG ZAB 2F mass spectrometer under normal conditions i.e. 8 kV accelerating voltage and source temperature \approx 150 °C. CAD spectra were obtained using helium as collision gas.

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